



Fast microwave-assisted catalytic pyrolysis of sewage sludge for bio-oil production



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HIGHLIGHTS

- A microwave-assisted system for catalytic pyrolysis of sewage sludge was developed.
- The optimal temperature and catalyst to feed ratio were determined.
- Mineral elements were concentrated in the bio-char after pyrolysis.
- HZSM-5 catalyst had good stability against deactivation during the pyrolysis process.

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ABSTRACT

In this study, fast microwave-assisted catalytic pyrolysis of sewage sludge was investigated for bio-oil production, with HZSM-5 as the catalyst. Pyrolysis temperature and catalyst to feed ratio were examined for their effects on bio-oil yield and composition. Experimental results showed that microwave is an effective heating method for sewage sludge pyrolysis. Temperature has great influence on the pyrolysis process. The maximum bio-oil yield and the lowest proportions of oxygen- and nitrogen-containing compounds in the bio-oil were obtained at 550 °C. The oil yield decreased when catalyst was used, but the proportions of oxygen- and nitrogen-containing compounds were significantly reduced when the catalyst to feed ratio increased from 1:1 to 2:1. Essential mineral elements were concentrated in the bio-char after pyrolysis, which could be used as a soil amendment in place of fertilizer. Results of XRD analyses demonstrated that HZSM-5 catalyst exhibited good stability during the microwave-assisted pyrolysis of sewage sludge.

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1. Introduction

Sewage sludge from municipal and industrial wastewater treatment plants is a great issue risking the environment and human health, and has raised growing concern recently (Fytilli and Zabaniotou, 2008; Laturnus et al., 2007). Nowadays, the most common methods for treatment and disposal of sewage sludge include landfill, agricultural application and incineration (Fonts et al., 2012). However, they all have drawbacks and have become less acceptable (Houillon and Jollet, 2005; Rio et al., 2006; Werther and Ogada, 1999). An alternative management technique is

pyrolysis which could achieve 50% reduction in waste volume (Inguanzo et al., 2002), the stabilization of organic matter, as well as the production of fuels. Elements such as Na and Mg will be concentrated in the pyrolysis char, which can then be used as the soil amendment or be upgraded to become an adsorbent (Bridle and Pritchard, 2004; Smith et al., 2009). The produced gas and oil can be either directly burned as a fuel to provide heat and electricity, or further converted to other chemicals through subsequent processes (Domínguez et al., 2006; Park et al., 2008).

Fonts et al. (2008) conducted pyrolysis of sewage sludge in a fluidized bed and obtained the maximum liquid yield of about 33 wt.% at the temperature of 540 °C with a solid feed rate of 3.0 g/min and nitrogen flow rate of 4.5 L/min. By using a quartz reactor, Sánchez et al. (2009) examined the effect of temperature increase from 350 to 950 °C on the composition of the oils obtained from sewage sludge pyrolysis and observed an increase in the

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concentration of mono-aromatic hydrocarbons and a strong decrease in the concentration of phenol and its alkyl derivatives. In order to improve the yield and quality of the bio-oil, many researchers used different catalysts in the pyrolysis of sewage sludge. Kim and Parker (2008) investigated the effect of zeolite on the product distribution from pyrolysis of different types of sewage sludges and concluded that zeolite did not improve oil and char yields due to the increased conversion of volatile matter to gas. However, Park et al. (2010) found that metal oxide catalysts (CaO and La₂O₃) contributed to a slight decrease in bio-oil yield but were significantly effective in removal of chlorine from the bio-oil.

Microwave based technology is an alternative heating method and has already been successfully used in biomass pyrolysis for biofuels production (Bu et al., 2012; Du et al., 2011; Wang et al., 2012). Microwave assisted heating has many advantages over conventional processes, which include: (1) Microwave can provide uniform internal heating for material particles since the electromagnetic energy is directly converted into heat at the molecular level (Sobhy and Chaouki, 2010). (2) Microwave heating is easier to control due to its instantaneous response for rapid start-up and shut-down. (3) The set-up of microwave system is simple, which facilitates its adaption to currently available large-scale industrial technologies. (4) It does not require high degree of feedstock grinding and can be used to handle large chuck of feedstock. (5) Microwave heating is a mature technology and the development of microwave heating system is of low cost. Despite many advantages of microwave heating over conventional heating methods and some progress made in biomass pyrolysis, only a few studies have been conducted on sewage sludge pyrolysis using microwave technology and the effects of catalyst on the pyrolysis process were not examined in their research (Domínguez et al., 2006; Menéndez et al., 2002).

In this study, microwave-assisted catalytic pyrolysis of sewage sludge was carried out with HZSM-5 as the catalyst for bio-oil production under different conditions. The effects of pyrolysis temperature and catalyst to feed ratio were investigated on product distribution and bio-oil composition. X-ray Diffraction (XRD) analyses of catalyst before and after reaction were conducted to examine its stability during pyrolysis process. In addition, characterization of bio-char was conducted using elemental analysis and ICP-OES multi-element determination.

2. Methods

2.1. Materials and catalysts

The sewage sludge used as the raw material for this study was obtained from the Metropolitan Wastewater Treatment Plant,

Saint Paul, Minnesota. The sewage sludge was a mixture of primary and secondary sludge. The basic physico-chemical characteristics of the sewage sludge including proximate analysis, elemental analysis and mineral elements determination are shown in Table 1. According to the elemental analysis, the simplified chemical formula of the raw material that derives is CH_{1.67}N_{0.10}O_{0.47}. The higher heating value (HHV) observed for sewage sludge is similar to that of other conventional and non-conventional fuels such as paper, wood, black liquor or low rank coal (Perry, 1984). It is reported that the presence of inorganic matter can influence the thermal decomposition process (Mohan et al., 2006; Oasmaa et al., 2010; Richards and Zheng, 1991). It can be seen from Table 1 that there are considerable amounts of P, Ca and K in the sewage sludge, whereas other metals such as Co, Ni, Cu and Zn are in lower proportions. Prior to use, the sewage sludge samples were ground using a rotary cutting mill and then screened to limit the particle size smaller than 2 mm. These ground samples were then dried for 72 h at 80 ± 1 °C.

A commercial zeolite, namely ZSM-5 (Si/Al = 30, surface area = 405 m²/g), in the ammonium form purchased from Zeolyst International (Conshohocken, PA) was used as the catalyst in the present study. Prior to use, the catalyst was calcined at 550 °C in air for 5 h to its active hydrogen form HZSM-5.

2.2. Apparatus

The tests of catalytic pyrolysis of sewage sludge were performed in a microwave oven (MAX, CEM Corporation), with the power of 750 W at a frequency of 2450 MHz. The schematic diagram of experimental apparatus is shown in Fig. 1. The system is composed of: (1) biomass feeder; (2) inlet quartz connector; (3) microwave oven; (4) quartz reactor; (5) microwave absorbent bed; (6) thermocouple (K-type) to measure the temperature of cavity; (7) thermocouple (K-type) to measure the temperature of bed particles; (8) outlet quartz connectors; (9) liquid fraction collectors; (10) condensers; (11) connection for vacuum pump. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage.

In this study, SiC particles with particle size of 30-grit were used as the microwave adsorbent bed, whose temperature could be increased very quickly with the microwave absorbed. Five hundred grams of SiC particles were first put in a quartz reactor, which was then placed in the cavity of the microwave oven. In order to maintain an inert atmosphere within the quartz reactor during pyrolysis, the system was vacuumed at 170 mm Hg for 10 min prior to the commencement of the microwave heating, with the vacuum being maintained during the entire heating process. The microwave oven was then turned on for heating process. For each experiment, the sample was prepared by physically mixing 15 g sewage

Table 1
Characteristics of sewage sludge.

Proximate analysis (wt.%)				Elemental analysis ^{a,b} (wt.%)				HHV ^d (MJ/kg)		NNHV ^e (MJ/kg)	
M	A ^a	V ^a	FC ^{a,c}	C	H	N	O ^c				
4.53	15.01	68.57	16.42	53.24	7.39	6.12	33.25	24.42		21.77	
Mineral elements ^a (mg/L)											
Al	As	B	Be	Ca	Cd	Co	Cr	Cu	Fe	K	
4188.5	6.2	22.4	0.36	20737.2	0.96	3.8	44.9	315.4	5108.5	6298.6	
Li	P	Mg	Mn	Mo	Na	Ni	Pb	Ti	V	Zn	
2.2	25641.3	5526.4	1153.0	5.0	1161.8	30.8	32.3	111.2	2.0	596.0	

M: moisture content; A: ash content; V: volatile matter content; FC: fixed carbon.

^a Dry basis.

^b Ash free basis.

^c Calculated by difference, FC (%) = 100 – A – V, O (%) = 100 – C – H – N.

^d Higher heating value, calculated using the equation (Vallios et al., 2009) HHV (MJ/kg) = 34.1 C + 123.9 H – 9.85 O + 6.3 N + 19.1 S.

^e Net heating value, calculated using the equation (Vallios et al., 2009) NHHV (MJ/kg) = (HHV – 21.92 H) (1 – MCWB/100) – 0.02452 MCWB, where MCWB is the moisture content on a wet basis of biomass.

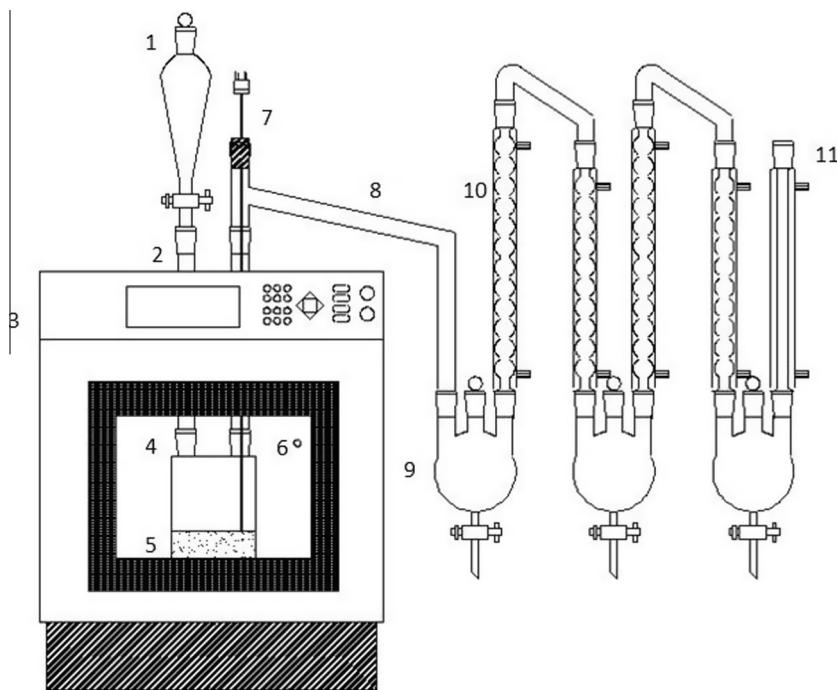


Fig. 1. Schematic diagram of microwave-assisted catalytic pyrolysis of sewage sludge.

sludge with a certain amount of catalyst. When the temperature of the SiC bed reached the set temperature, the prepared sample was introduced into the reactor through the feeder and the pyrolysis reaction occurred once the sample was dropped onto the hot bed. At the same time, the microwave oven was set to be on or off in order to maintain a stable temperature of the adsorbent bed. Flowing through the condensers, the condensable components in the product were condensed and collected into the liquid collectors as bio-oil for subsequent analysis. The residue in the reactor after pyrolysis was collected as bio-char. The yields of bio-oil and bio-char were calculated on the basis of their actual weight, while the gas yield was calculated by difference based on the mass balance.

2.3. Oil and char analysis

The composition of bio-oil was determined using an Agilent 7890–5975C gas chromatography/mass spectrometer (GC/MS) with a HP-5 MS capillary column. Helium was used as the carrier gas at a flow rate of 1.2 mL/min. The injection size was 1 μ L with a split ratio of 1:10. The oven temperature was 40 °C initially held for 3 min and then increased to 290 °C at a rate of 5 °C/min, and held at 290 °C for 5 min. The temperatures of injector and detector were maintained at 250 and 230 °C, respectively. The compounds were identified by comparing their mass spectra with those from the National Institute of Standards and Technology (NIST) mass spectral data library. Calibration was not carried out due to the large number of compounds in the pyrolysis bio-oil. A semi-quantitative method was used to determine the relative proportion of each compound in the oil by calculating the chromatographic area percentage.

For the characterization of bio-char, elemental analysis was conducted to determine the contents of C, H, N and O, using an Exeter Analytical Inc. (EAI) CE-440 elemental analyzer. In addition, inductively coupled plasma-optical emission spectrometry (ICP-OES) multi-element determination was carried out on an Applied

Research Laboratories (ARL) 3560 optical emission spectrometer to determine the contents of other mineral elements including K, Ca, Mg, Fe, etc.

2.4. Catalyst characterization

The X-ray powder diffraction (XRD) patterns, obtained on a Bruker-AXS (Siemens) D5005 X-ray diffractometer instrument with a Cu K α radiation at 45 kV and 40 mA, were used to identify the major crystalline phases present in the catalysts. Data collected from the instrument were analyzed using software MDI Jade 8.0.

3. Results and discussion

3.1. Effect of pyrolysis temperature on bio-oil production

The effect of pyrolysis temperature on the yield and composition of the bio-oil was investigated at temperatures ranging from 450 to 600 °C, with the catalyst to feed ratio being 2:1. As shown in Fig. 2, temperature has great influence on product distribution from the sewage sludge pyrolysis. The oil yield increased with the pyrolysis temperature and reached a maximum yield of 20.9 wt.% at the temperature of 550 °C. A decrease in oil yield was observed when the temperature increased above 550 °C. For the yield of bio-char, a continuous decrease was found when the temperature increased from 450 to 600 °C. The formation of bio-oil was mostly due to the devolatilization of organic matter in the sewage sludge, which was promoted by higher temperature as there was more energy available to break the strong organic bonds. This is the main reason for the initial increase in bio-oil yield with increasing temperature. The decrease in oil yield above the optimal temperature was probably because of the secondary reactions such as thermal cracking of the volatile compounds. Thermal cracking is an endothermic reaction and was reported to become significant at temperatures higher than approximately 500 or 550 °C (Encinar et al., 2000). This can also explain the

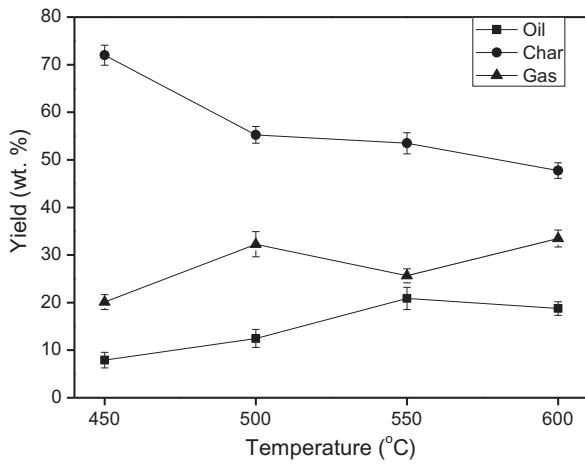


Fig. 2. Effect of temperature on product distribution from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, catalyst to feed ratio: 2:1.

increase in gas yield when the temperature reached above 550 °C. In addition, the occurrence of carbonization of volatiles for char-coal is another possible reason for the decrease in oil yield. Since the ash content of sewage sludge is always high, the bio-oil yield is usually expressed on ash free basis, which is 24.4 wt.% at 550 °C in this study. Similar results were obtained through sewage sludge pyrolysis in a fluidized bed reactor (Fouts et al., 2008) and in a fixed bed reactor under both CO₂ and N₂ atmospheres (Jindarom et al., 2007).

The chemical composition of bio-oil is also influenced by temperature. As shown in Fig. 3, the trends for the effect of temperature were different on the different chemical families present in the oil. The proportions of aliphatic hydrocarbons, aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) increased with temperature and reached the maximum at 550 °C. In contrary, the proportions of oxygen-containing aliphatic compounds, nitrogen-containing aliphatic compounds and nitrogen-containing aromatic compounds decreased with increasing temperature and reached the minimum at 550 °C. For oxygen-containing aromatic compounds, the proportion decreased with temperature initially and reached the minimum at 500 °C, and then increased when the temperature continued to rise. From the perspective of bio-oil composition, the optimal temperature for microwave-assisted catalytic pyrolysis of sewage sludge was 550 °C since under this

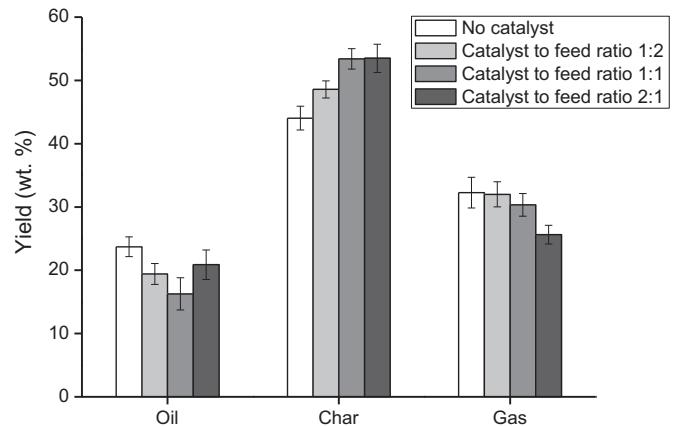


Fig. 4. Effect of catalyst to feed ratio on product distribution from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, pyrolysis temperature: 550 °C.

temperature, the highest proportions of aliphatic and aromatic hydrocarbons and the lowest proportions of oxygen- and nitrogen-containing compounds were obtained in the pyrolysis bio-oil, making it more suitable to be used as a fuel or feedstock for the production of valuable chemical products. The most dominant compounds in the bio-oil included naphthalene (9.5%), *p*-xylene (8.8%), 1,3,5-trimethyl-benzene (8.0%), 1-methyl-naphthalene (7.1%), 1-ethenyl-3-methylene-cyclopentene (6.6%) and indene (5.6%), which all belong to important chemical intermediates or precursors to other chemicals, or can be used as a solvent for chemical reactions. The same conclusion that the maximum proportion of aliphatic hydrocarbons in the pyrolysis oil could be obtained at 550 °C was reached by Fouts et al. (2009) and Jindarom et al. (2007) in a fluidized bed reactor and a fixed bed reactor, respectively. However, the trends of proportion for other chemical families were different than previous studies (Fouts et al., 2009; Jindarom et al., 2007; Park et al., 2008; Sánchez et al., 2009).

3.2. Effect of catalyst to feed ratio on bio-oil production

Previous research in catalytic pyrolysis of sewage sludge was very limited (Beckers et al., 1999; Fouts et al., 2012; Kim and Parker, 2008). The use of catalyst in sewage sludge pyrolysis and

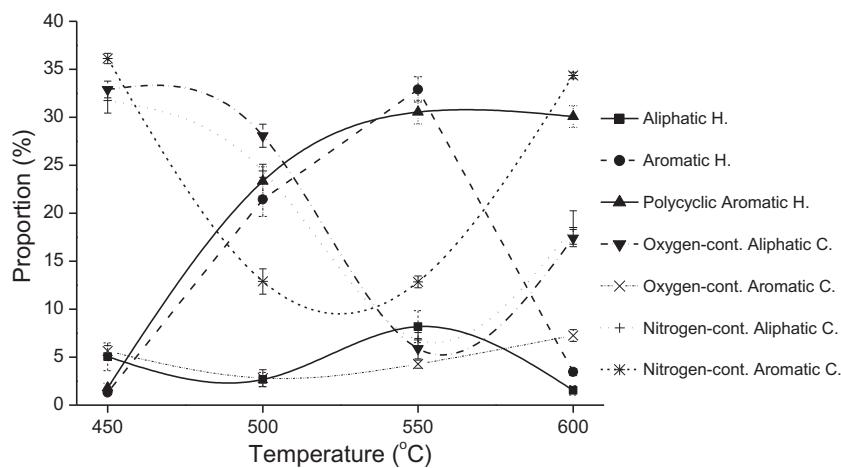


Fig. 3. Effect of temperature on bio-oil composition from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, catalyst to feed ratio: 2:1.

the effects of catalyst to feed ratio on bio-oil yield and composition were investigated in this study. As shown in Fig. 4, the use of catalyst in the pyrolysis resulted in a slight decrease in oil yield. This is probably because the pyrolysis vapors had to pass through the catalyst particles, increasing the gas residence time. Consequently, the thermal cracking and carbonization reactions of volatiles occurred with higher probability, which would reduce the bio-oil yield. This explanation can be confirmed by the increase in the char yield when catalyst was used in the sewage sludge pyrolysis process. However, the oil yield increased and the gas yield decreased as the catalyst to feed ratio increased from 1:1 to 2:1. A possible reason was that the short-chain gas molecules from thermal cracking of volatiles recombined on the catalyst and underwent a series of aromatization, alkylation and isomerization reactions to produce aliphatic and aromatic compounds, increasing the bio-oil yield. From the perspective of product distribution, catalyst does not improve the bio-oil yield. The study of sewage sludge pyrolysis in a laboratory-scale horizontal batch reactor conducted by Kim and Parker (2008) demonstrated a decrease in liquid yield when the catalyst to feed ratio increased over 1.5. The authors attributed such a decrease to an increase in the catalytic cracking reactions, which resulted in increased conversion of volatiles to gas.

Fig. 5 presents the effect of catalyst to feed ratio on bio-oil composition from microwave-assisted pyrolysis of sewage sludge at 550 °C. It can be seen that although the proportion of aliphatic hydrocarbons in the bio-oil did not change too much with catalyst, significant increase in proportion of aromatic hydrocarbons was observed from catalytic pyrolysis compared with non-catalytic pyrolysis. This is consistent with previous studies on lignocellulosic biomass showing that the organics derived in the pyrolysis process could be deoxygenated and cracked to produce aromatics over the HZSM-5 catalyst (Mihalcik et al., 2011; Mullen and

Boateng, 2010). The reaction mechanism and pathways can be illustrated using those postulated for the catalytic pyrolysis of carbohydrates and lignocellulosic biomass on HZSM-5 (Carlson et al., 2010; Williams and Horne, 1994). Carbohydrate derived organics, including alcohols, ketones, aldehydes and acids, were deoxygenated and cracked into C2–C6 olefins, which were transformed to benzene through a series of aromatization reactions. Benzene could be converted to other aromatics through alkylation and isomerization reactions. This was consistent with the decrease in the proportion of oxygen-containing aliphatic compounds in the bio-oil. In addition, the proportions of nitrogen-containing aliphatic and aromatic compounds were also decreased with catalyst, which was not mentioned in previous studies and needs further investigation. The proportions of oxygen- and nitrogen-containing compounds decreased significantly when the catalyst to feed ratio increased from 1:1 to 2:1. This was probably because the surface contact between the pyrolysis vapors and catalyst particles was not adequate when the catalyst to feed ratio was 1:1.

3.3. Analysis of bio-char

The elemental analysis and ICP-OES multi-element determination were carried out for the bio-char from microwave-assisted pyrolysis of sewage sludge at 550 °C. The contents of C, H and N in the bio-char were 46.6%, 3.1% and 5.3%, respectively. The carbon content of bio-char from sewage sludge pyrolysis was lower than that from lignocellulosic biomass pyrolysis (Borges et al., 2014), which was probably due to the high ash content of sewage sludge.

Table 2 shows the contents of mineral elements in the bio-char. It can be seen that the contents of P, Ca, K and Mg which belong to essential elements to plants were very high, whereas the hazardous heavy metals including Cd, As, Ti and Pb were in very low proportions. Comparing the results in Tables 1 and 2, it can be concluded that the essential elements were concentrated in the bio-char after the pyrolysis process. Therefore, in addition to the use for adsorbent and fuel production, bio-char can be used as a soil amendment to achieve mineral recovery and increase soil fertility. Bio-char addition to soil can improve crop yield through reducing nutrient leaching and soil acidity, as well as enhancing the crop uptake of the essential nutrients. In addition, returning bio-char into soil reduces the need for fertilizers, thereby reducing the agricultural cost and environmental pollution caused by the fertilizer production and application.

3.4. Catalyst characterization

The HZSM-5 catalysts before and after pyrolysis reactions under different temperatures were characterized and compared using X-ray diffraction (XRD) technique to determine the effect of microwave-assisted pyrolysis process on the catalyst structure. The results showed that the primary diffraction peaks of the HZSM-5 catalyst occurred at the diffraction angles of 23.2°, 23.9° and 24.5°. The main crystalline phase existing in the catalyst was silicon-aluminum compound $\text{Al}_2\text{O}_3\text{-}54\text{SiO}_2$ which was obtained through data analysis using the Jade 8.0. Comparing the XRD patterns of catalysts before and after pyrolysis reactions, little change

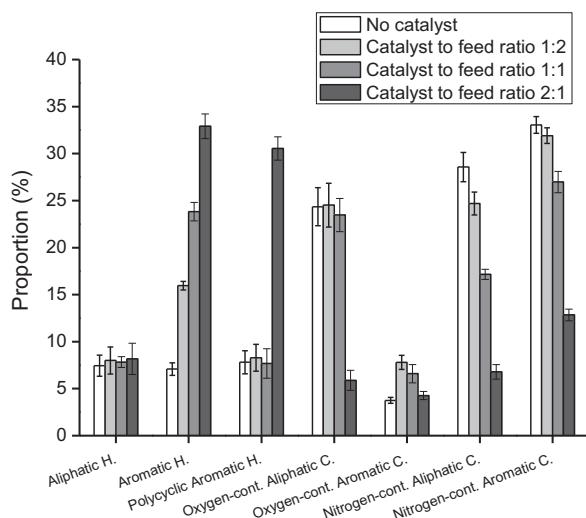


Fig. 5. Effect of catalyst to feed ratio on bio-oil composition from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, pyrolysis temperature: 550 °C.

Table 2

Contents of mineral elements in bio-char from microwave-assisted pyrolysis of sewage sludge at 550 °C.

Mineral elements (mg/L)										
Al	As	B	Be	Ca	Cd	Co	Cr	Cu	Fe	K
9522.7	4.8	40.8	0.35	44401.5	2.6	8.2	114.4	623.5	7710.2	11364.0
Li	P	Mg	Mn	Mo	Na	Ni	Pb	Ti	V	Zn
3.7	53362.0	11842.0	2528.1	12.2	2542.0	79.0	72.0	49.7	5.2	1305.0

Table 3

Comparison of peak areas and crystallite sizes at characteristic diffraction angles of HZSM-5 XRD patterns before and after pyrolysis reactions under different temperatures

Catalyst	Area (a.u.)			Crystallite size (Å)		
	23.2°	23.9°	24.5°	23.2°	23.9°	24.5°
Fresh catalyst	6679	3563	1100	224	181	373
450 °C	6043	3365	958	224	185	374
500 °C	7183	4002	1678	244	184	279
550 °C	6825	3274	1240	247	216	351
600 °C	5651	3436	1232	239	164	293

of phase composition and crystalline structure on catalyst was observed for all the temperatures studied. It demonstrated that the HZSM-5 catalyst had good stability during the microwave-assisted pyrolysis process towards deactivation caused by coking or sintering.

The peak areas and crystalline sizes at the characteristic angles (23.2°, 23.9° and 24.5°) of HZSM-5 XRD patterns before and after pyrolysis reactions are shown and compared in Table 3. It can be seen that there is no obvious difference between peak areas of fresh catalyst and catalysts after reaction under different temperatures except at 500 °C. For the crystalline size estimated by the Scherrer equation, no significant increase was found for catalysts after reactions, even at 600 °C. It means that the HZSM-5 catalyst could stand high temperatures with negligible deactivation by coking and sintering, which was probably due to the short time on stream for the fast microwave-assisted pyrolysis process. Therefore, it can be concluded that HZSM-5 has good stability and is a suitable catalyst for the microwave-assisted catalytic pyrolysis of sewage sludge.

4. Conclusions

In this study, a microwave-assisted system has been developed and used for catalytic pyrolysis of sewage sludge for bio-oil production. This study shows that microwave heating is effective for sewage sludge pyrolysis. The optimal temperature and catalyst to feed ratio for bio-oil production were 550 °C and 2:1, respectively. The lowest proportions of oxygen- and nitrogen-containing compounds in the bio-oil were achieved under the optimal conditions. The bio-char after pyrolysis contained considerable amounts of mineral elements and could be used to improve soil fertility. Catalyst characterization indicated good stability of HZSM-5 catalyst against deactivation during the pyrolysis process.

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